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THE ROLE OF GRAIN BOUNDARIES IN HYDROGEN DIFFUSION IN METALS AT 25 °C

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The effect of grain size on hydrogen diffusion at 25 °C has been examined for 4340 steel (body-centered cubic) and for Inconel 718 (face-centered cubic). It has been found that the effect of grain size is important for body-centered cubic structures, but plays a much less important role in face-centered cubic structures. Accurate measurements of hydrogen desorption coefficients during hydrogen desorption show that these are not greatly different for both types of structures.

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INTRODUCTION

There has been considerable debate in recent years regarding the role of grain boundaries in hydrogen diffusion in metals. In pure iron, which has a body-centered cubic (BCC) structure, grain boundary trapping has not been observed either by autoradiography or by the diffusion technique.[1 2] Diffusivities were found to be independent of grain size. On the other hand, evidence has been found for grain boundary diffusion, trapping, and dislocation transport of hydrogen in austenitic face-centered cubic (FCC) stainless steels[3–19] by both radiographic and diffusion techniques.

It has been observed in this laboratory that, at 25 °C, BCC structures allow hydrogen penetrations on charging which are greater than those which would be predicted by diffusion theory (nonuniform hydrogen distribution), while the penetrations in FCC structures are in close compliance with diffusion theory.[20–23] Two possibilities exist which might explain these differences between the BCC and FCC structures. One possibility is that grain boundaries act as an aid to the penetration of hydrogen in the BCC structures. Grain sizes are generally very small in these structures, so that there is much more intergranular surface available. The other possibility is that there are more interstitial sites available for hydrogen occupation in the BCC metal lattice if hydrogen penetration is primarily through the crystal lattice. In the FCC lattice, there is one such site available for hydrogen per metal atom; while in BCC structures, there are 1.5 sites per metal atom.

Because of the noncompliance of hydrogen penetrations in BCC structures with diffusion theory and to determine the role of grain boundaries, if any, in this phenomenon, it seemed desirable to study initial hydrogen concentration profiles after charging in both BCC and FCC metal structures. Therefore, two different alloys—4340 steel (BCC) and Inconel 718 (FCC)—were examined using an electrochemical technique to measure hydrogen diffusion. For each alloy, two widely differing grain sizes were used. Results of this work are presented in this report.

EXPERIMENTAL

Mobile hydrogen concentrations were determined electrochemically, using cylindrical samples 2.54-cm long with a radius of 0.3175 cm. Samples were drilled and tapped on one end to accept a 3-48 thread, as required by the sample holder. Flat samples with a 1.5875-cm diameter and 0.159-cm thickness were used for accurate determination of diffusion coefficients, since the geometry of that configuration is more ideal for this purpose. Sample holders for flat and cylindrical samples are shown in figures 1 and 2, respectively. Samples were electrolytically charged at 25 °C in 0.1N sulfuric acid (H_2SO_4) at a current density of 40 mA/cm^2.

Sample blanks were run at a constant potential of 0.0V (saturated calomel electrode) in a 0.1N sodium hydroxide (NaOH) solution at 25 °C. The period of measurement for all samples was 150,000 s,

with data points (current versus time) being recorded every 500 s. Data for hydrogen containing samples were collected in the same manner, with currents due only to hydrogen being obtained by subtraction of the currents for blanks. After each experiment, the current versus time data were read to an IBM PC/AT computer for calculation. Methods for data reduction to obtain coulombs of hydrogen desorbed versus time and initial concentration profiles for both cylindrical[21] and flat[20] samples have been described. The computer program PDEONE[24 25] was used for all theoretical calculations.

Since it was desirable to obtain samples of 4340 steel with as few grains as possible, an attempt was made to obtain single crystals of this metal by recrystallization. The attempt failed to produce a single crystal, but resulted in obtaining metal with very large grains and, as a result, much less inter-granular surface. Photographs of the magnified grain structure in both normal wrought and recrystallized 4340 steel are shown in figures 3 and 4, respectively. The average grain size in the recrystallized 4340 steel (200 μm) was about four times as large as that of the normal steel (50 μm). An x-ray diffraction pattern of the 4340 steel was taken which showed all reflections for the BCC lattice to be present.

Samples of Inconel 718 with very fine grains were obtained by first cold working the solution-treated alloy and then aging it. Photographs of the magnified grains structures, in both normal (solution treated and aged) and cold worked and aged Inconel 718, are shown in figures 5 and 6, respectively. Grain sizes in the normal metal (60 μm average) were approximately three times as large as those of the cold-worked alloy (20 μm average). Thus, considerably more intergranular surface exists in the cold-worked Inconel 718.

RESULTS AND DISCUSSION

4340 Steel

The hydrogen desorption curves for normal wrought and recrystallized 4340 steel are shown in figures 7 and 8, respectively. As in other BCC structures, the normal material shows a high degree of uniformity (constant hydrogen concentration through bulk) at 50.7 percent. Thus, hydrogen penetration on charging is much greater than that predicted by diffusion theory.

The curves for the recrystallized concentration through bulk 4340 steel show that hydrogen desorption obeys diffusion theory completely. The hydrogen concentration profiles in the metal obtained initially on charging are shown in figure 11. The center of the cylinder is at $r = o$, with the surface at $r =$ 0.3175 cm. The curve for normal 4340 steel exhibits much greater penetration than diffusion theory would predict. The curve for recrystallized 4340 steel is completely in accord with diffusion theory. Thus, the intergranular surface available apparently plays a very important role in BCC structures. Diffusion coefficients at 25 °C are 2.29×10^{-8} cm^2/s for the normal 4340 steel and 1.88×10^{-8} cm^2/s for the recrystallized steel. Thus, the diffusion coefficient for the normal steel is slightly greater than that for the recrystallized steel, although the results are within the experimental error (about $\pm0.30\times10^{-8}$ cm^2/s).

Inconel 718

Hydrogen desorption curves for cold-worked Inconel 718 are shown in figure 9, while those for the normal alloy are shown in figure 10. The cold-worked alloy has a uniformity of 19.6 percent, while

that for the normal alloy shows a uniformity of 11.4 percent. Thus, there is a slight effect due to grain size, but both percent uniformities are low, as are those for other FCC structures, including single crystals. The hydrogen concentration profiles obtained initially after charging at 25 °C are shown in figure 12 for normal and cold-worked Inconel 718. The difference in the profiles is quite small and barely distinguishable, and indicates that the effect of grain boundaries is much less important in the FCC metals.

The diffusion coefficient obtained for normal Inconel 718 is 1.88×10^{-8} cm^2/s , while that for the cold-worked material is 3.78×10^{-8} cm^2/s . Thus, the diffusion coefficient for the cold-worked material, with more intergranular surface available, is larger than that for the normal material. However, the difference is not that great, although it is greater than the experimental error.

These results for Inconel 718, therefore, appear to be in disagreement with those of previous investigators, who concluded that intergranular diffusion played a rather important role in the FCC structures.

CONCLUSIONS

The results of this investigation suggest that grain boundary diffusion in 4340 steel plays an important role in the absorption of hydrogen on charging at 25 °C. Hydrogen penetrations on charging BCC structures at 25 °C have previously been found in this laboratory to be much greater than those which would be predicted by diffusion theory. On the other hand, grain boundary diffusion plays a much less important role in Inconel 718, and hydrogen concentration profiles are found to closely follow the diffusion theory. These results are consistent with other FCC alloys studied in this laboratory.

Accurate measurements of diffusion coefficients during hydrogen desorption indicate a small effect by grain boundaries in both FCC and BCC structures. Diffusion coefficients for the alloys with more intergranular surface are generally larger than those with less surface, but differences in their values are not much larger than the experimental error.

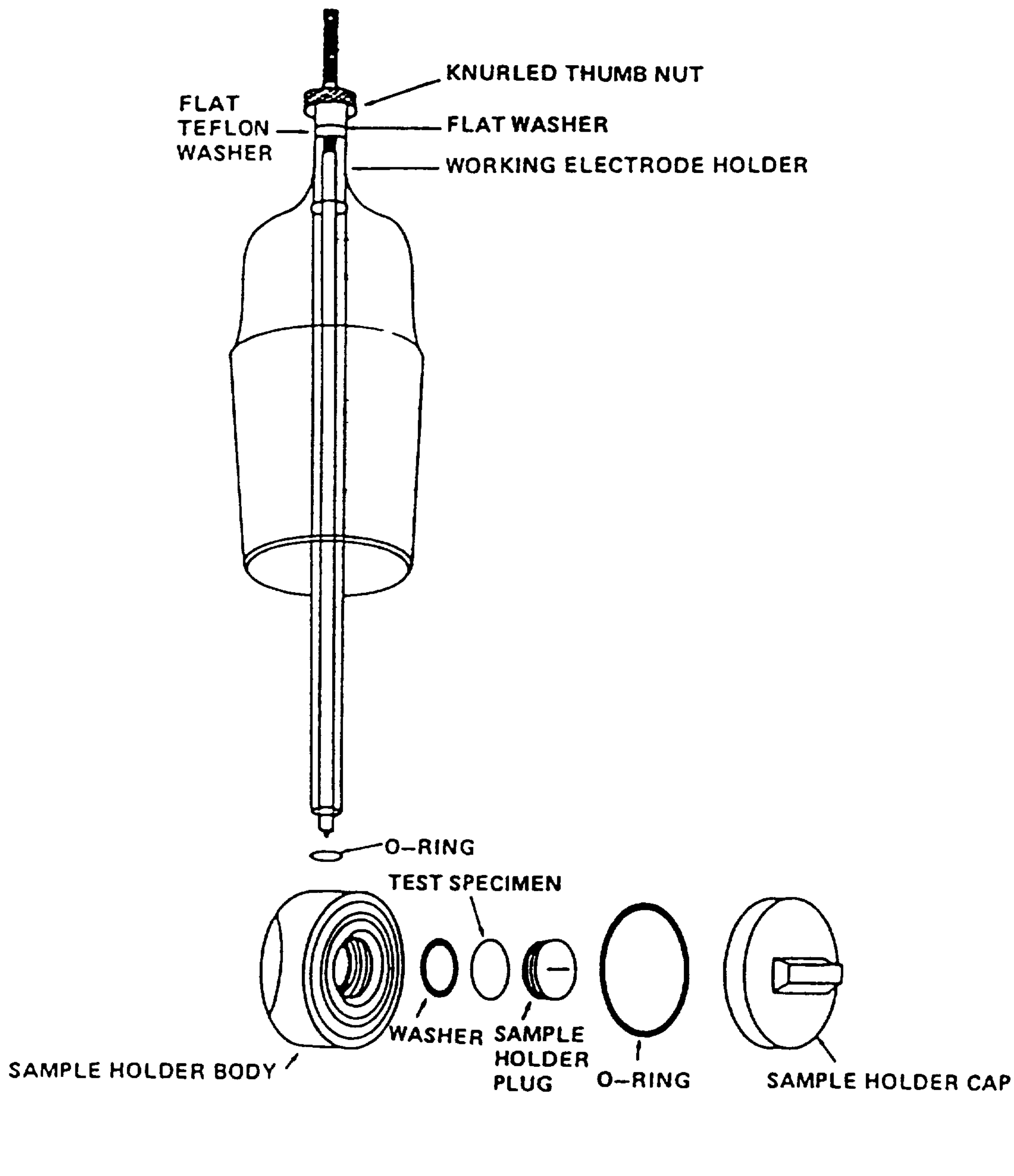

Figure 1. Exploded view of flat sample holder.

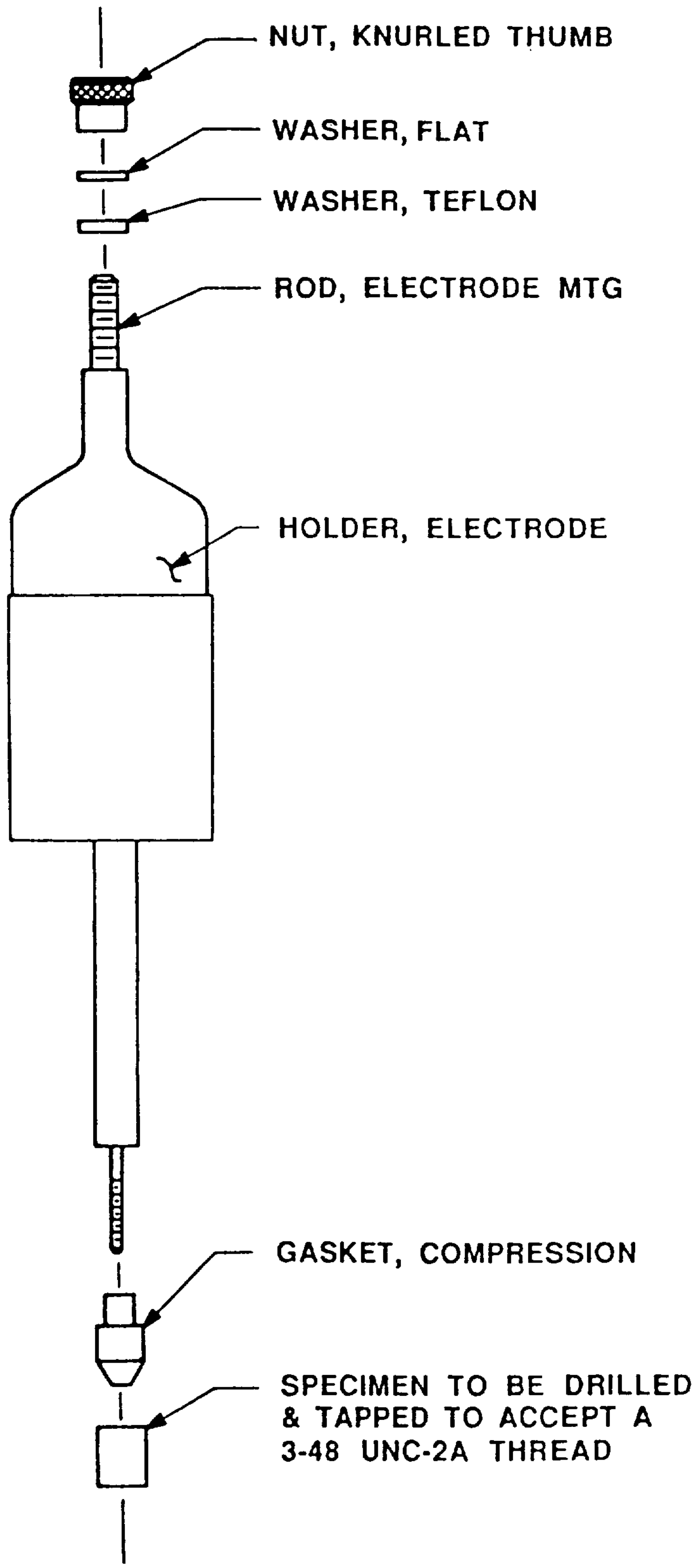

Figure 2. Sample holder for cylindrical samples.

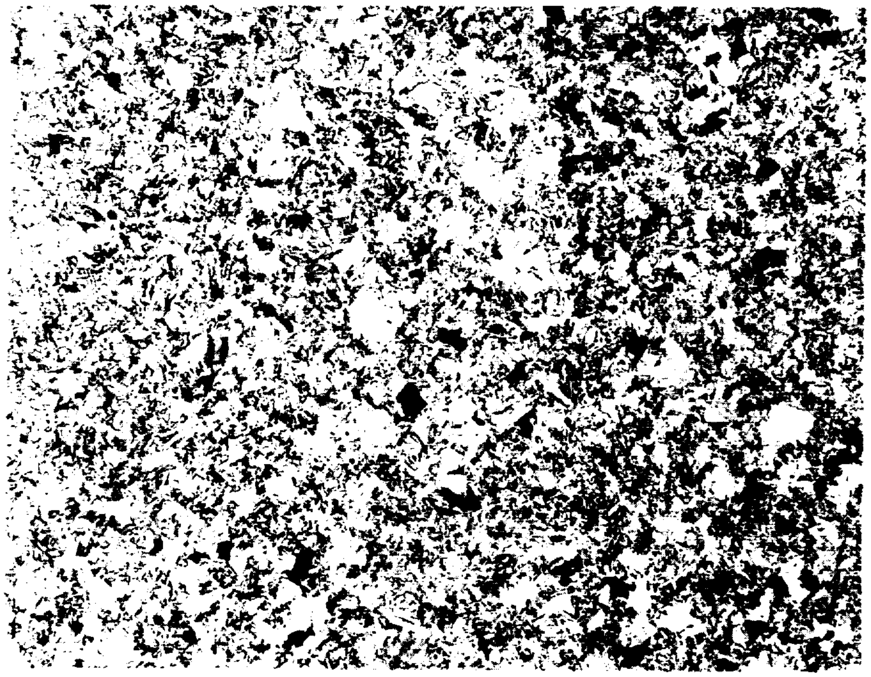

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Figure 3. Grain structure in normal wrought 4340 steel.

× 100

Figure 4. Grain structure in recrystallized 4340 steel.

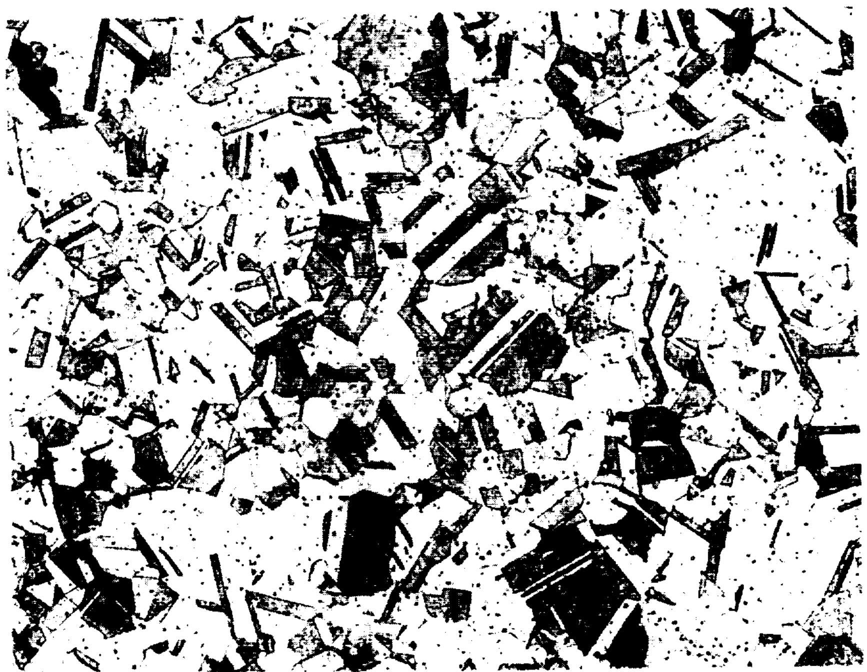


Figure 5. Grain structure in Inconel 718.

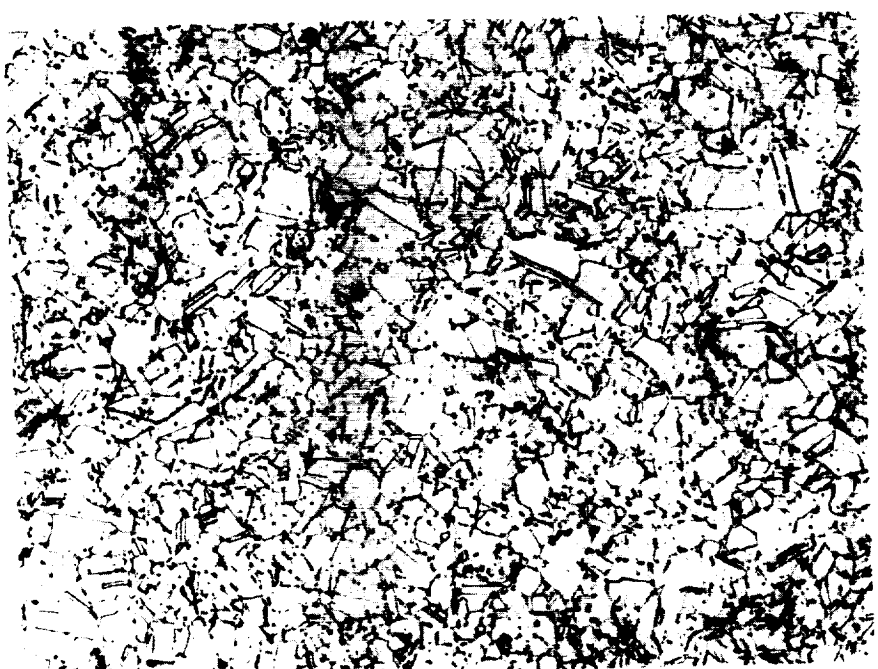


Figure 6. Grain structure in cold-worked Inconel 718.

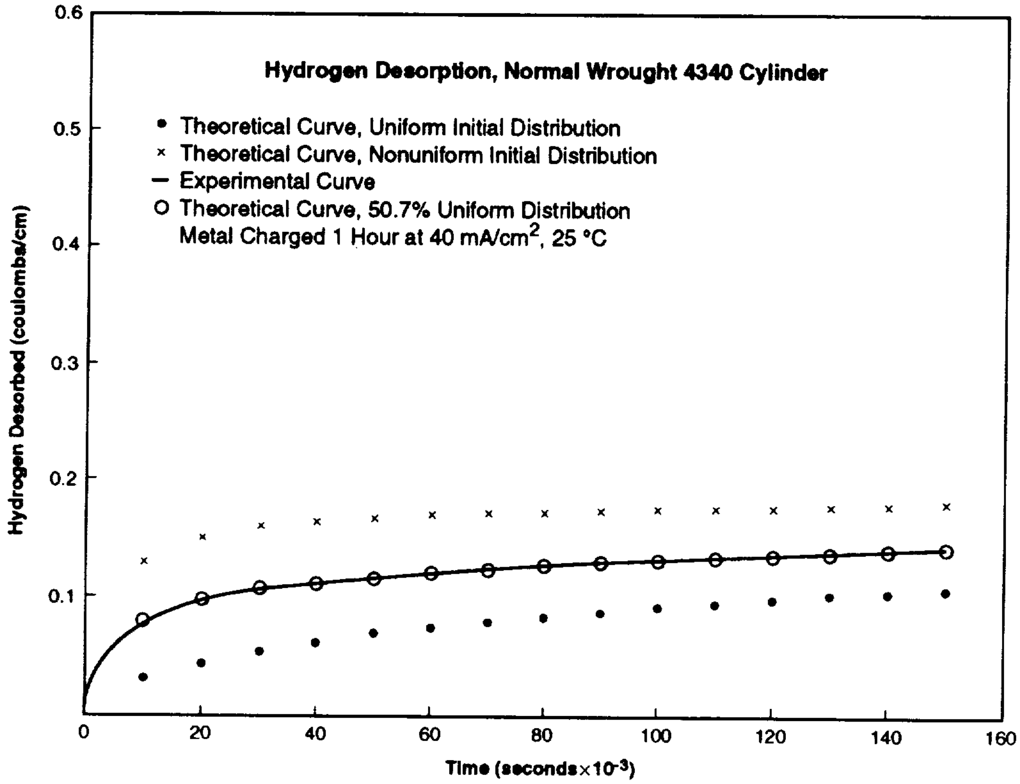


Figure 7. Hydrogen desorption curves for normal wrought 4340 steel charged at 25 °C.

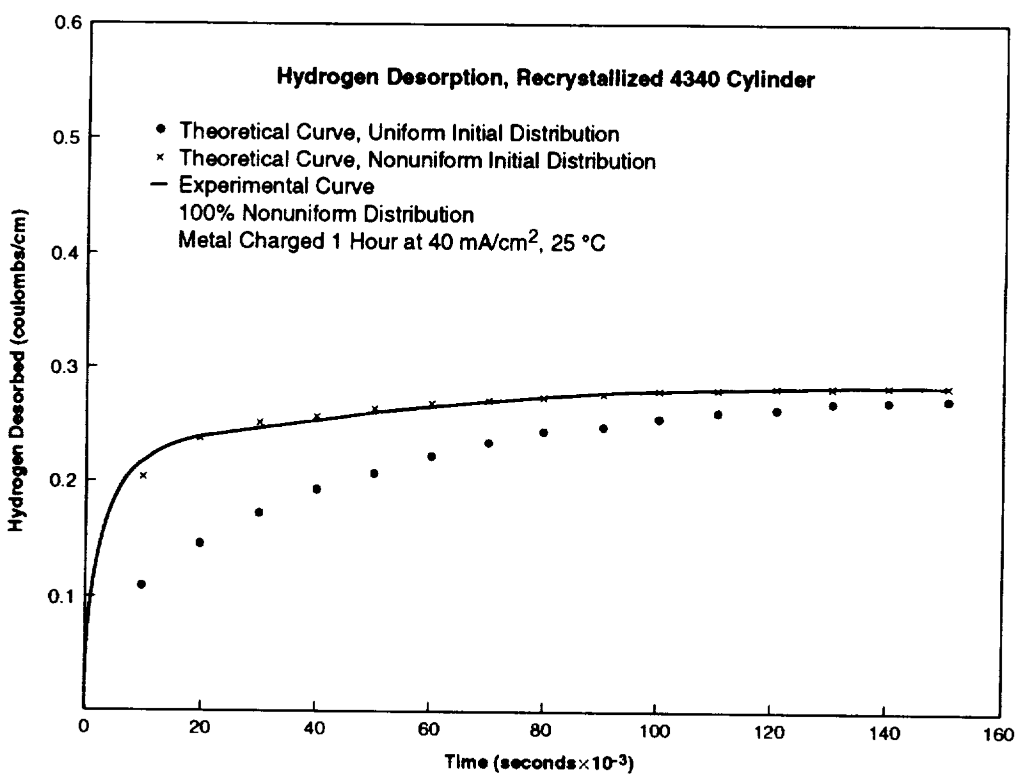
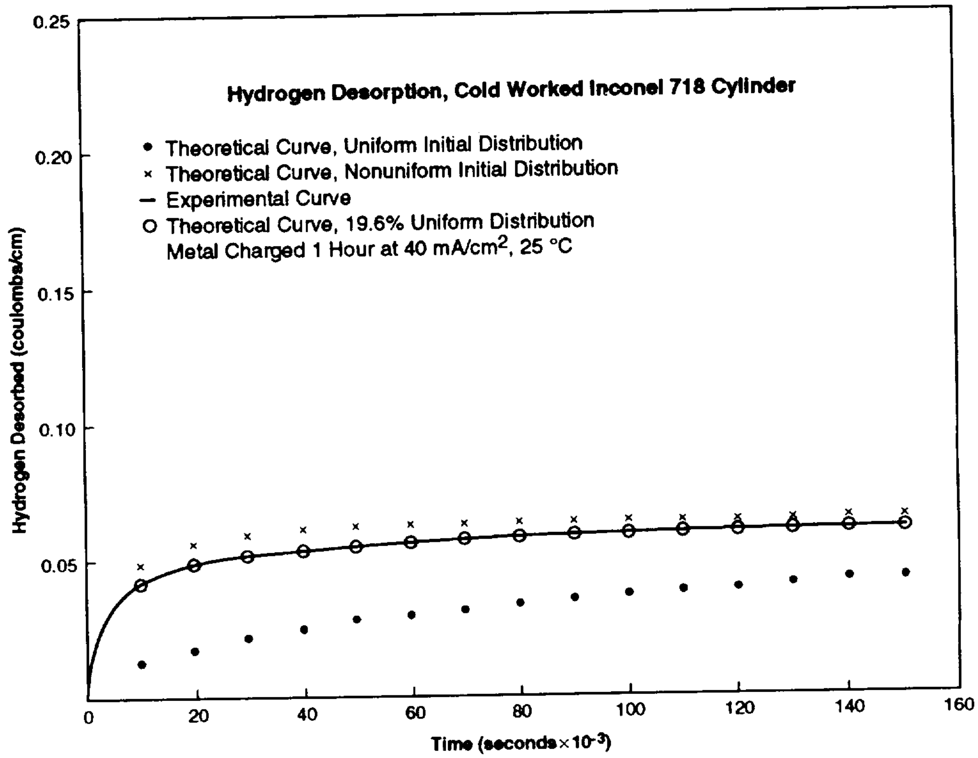


Figure 8. Hydrogen desorption curves for recrystallized 4340 steel charged at 25 °C.



'igure 9. Hydrogen desorption curves for cold-worked Inconel 718 charged at 25 °C.

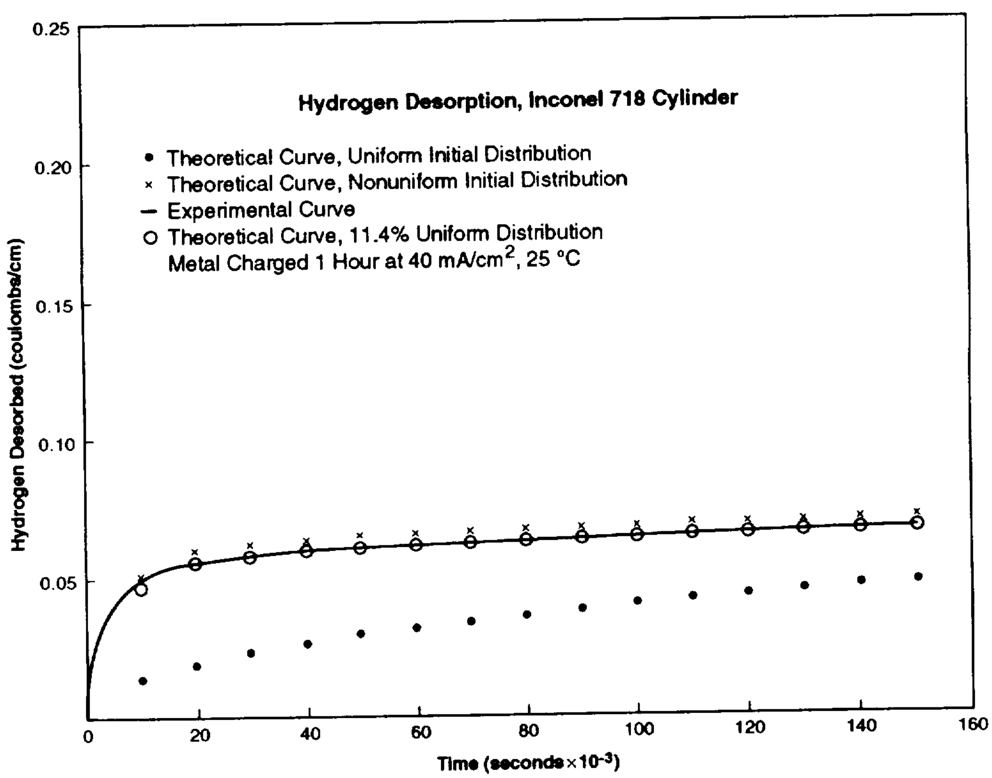


Figure 10. Hydrogen desorption curves for Inconel 718 charged at 25 °C.

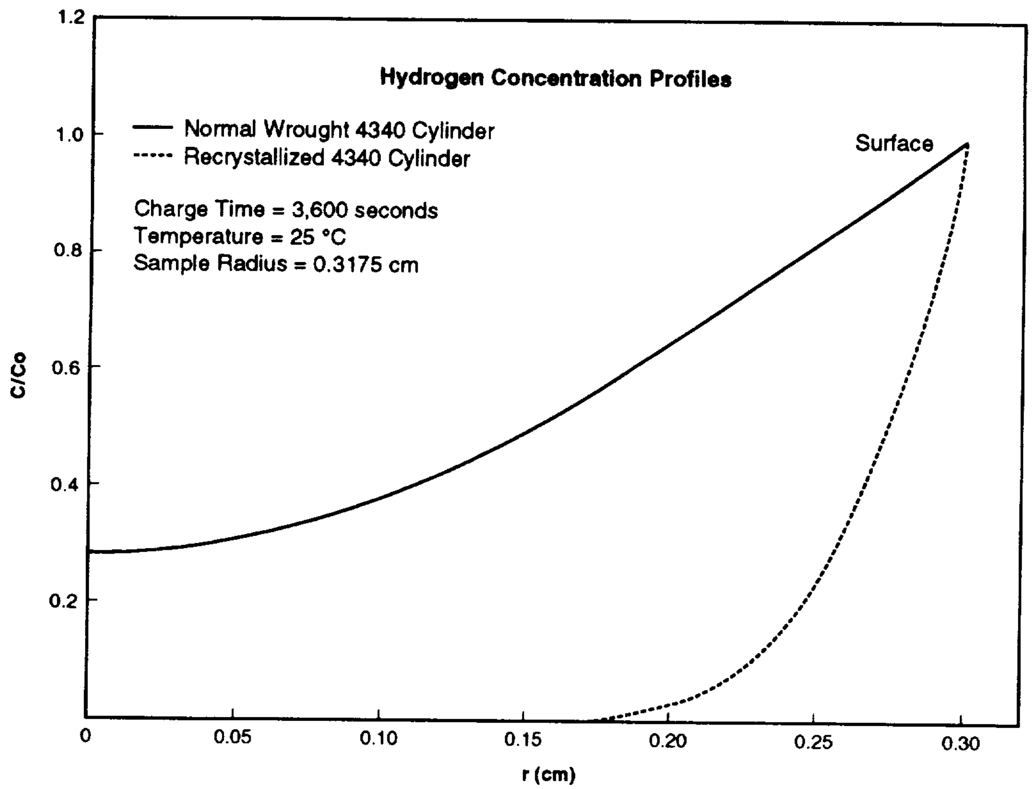


Figure 11. Hydrogen concentration profiles for normal wrought and recrystallized 4340 steel.

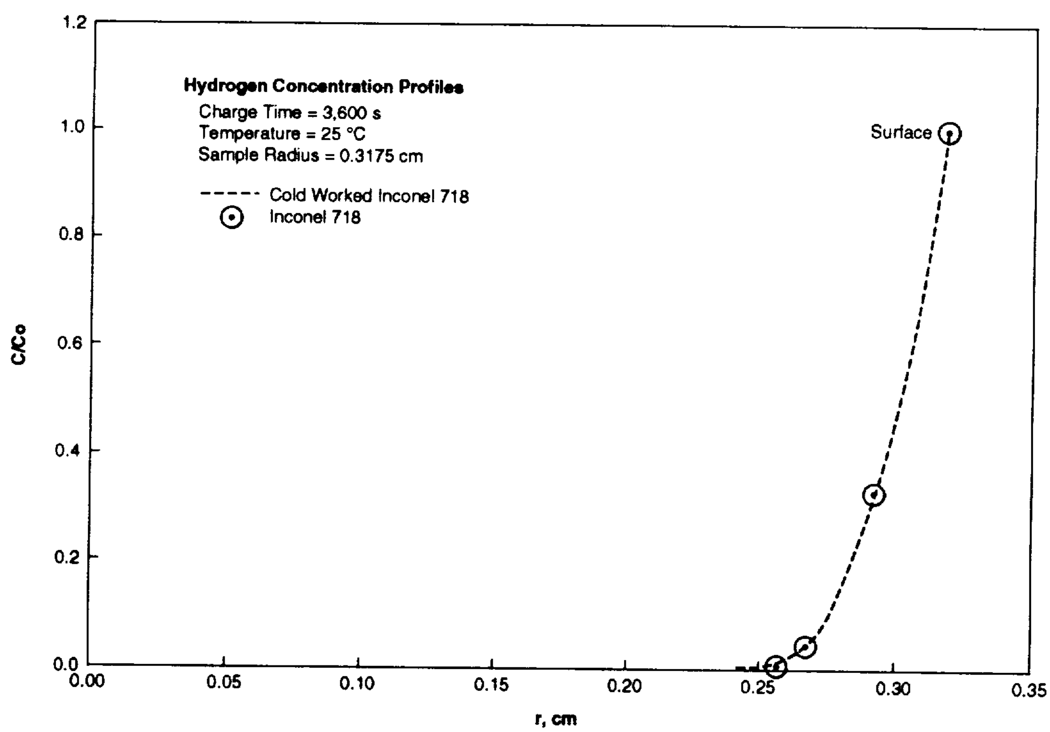


Figure 12. Hydrogen concentration profiles, Inconel 718 and cold-worked Inconel 718.

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APPROVAL

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The information in this report has been reviewed for technical content. Review of any information concerning the Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

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